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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	ampere	kg	kilogram
°C	degree Celsius	L	liter
gal	gallon	lb	pound
gpm/ft^2	gallon per minute per square foot	mL	milliliter
		min	minute
g	gram	ppm	part per million
g/L	gram per liter	pct	percent
hp	horsepower	yr	year
h	hour		
in	inch		

USING SOLVENT-IMPREGNATED CARBON TO RECOVER COPPER FROM OXIDIZED MILL TAILINGS

By T. H. Jeffers [1] and R. D. Groves [2]

ABSTRACT

The Bureau of Mines conducted laboratory tests to devise a procedure for extracting copper from low-grade discarded mill tailings. A solid extractant consisting of an organic solvent extraction reagent adsorbed on granular activated carbon was investigated and proved to be satisfactory for extracting copper directly from leach pulps. When this material was used in a cyclic leaching, stripping, and electrowinning process, 95 pct of the acid-soluble copper was recovered from oxidized mill tailings. The weathered tailings contained 0.24 pct Cu (total) and 0.20 pct acid-soluble Cu. The copper was recovered as cathodes containing, in parts per million, 1.6 Pb, 3.6 Fe, 0.5 Sb, 1.5 Al, 1.9 Mn, and <1 Mg.

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INTRODUCTION

Copper has traditionally been recovered from sulfide ores by a series of steps: fine grinding, flotation of sulfide minerals, smelting, and refining to electrolytic copper. These ores often contain small amounts of oxidized copper minerals that are not recovered by flotation and are discarded with the mill tailings. Additionally, weathering action on the discarded tailings has oxidized much of the remaining sulfide minerals. During the past 50 yr, over 5 billion tons of tailings containing 5 to 6 million tons of copper have accumulated in copper mining districts of the United States (1-2).[3] These tailings remain an untapped and potential source of copper.

The oxidized copper in mill tailings is readily soluble in dilute acid but conventional copper recovery processes require clarified leach solutions. Because most tailings are low grade, costly liquid-solid separation techniques to produce clarified solutions are not practical. One method that has been used to recover copper from leached pulps is the leach-precipitation-flotation (LPF) process (3-4). In this process, sponge iron is added to the pulp to precipitate cement copper, and the cement copper is recovered by flotation. The liquid-solid separation step is avoided but costly sponge iron is consumed.

The Bureau of Mines investigated the effectiveness of solvent-impregnated carbon in a resin-in-pulp (RIP) process to recover copper from mill tailings. RIP processes have been used by the uranium industry to avoid liquid-solid separations (5). In these processes, ion exchange resins are added to the leach pulp to adsorb the dissolved uranium, the loaded resins are recovered by screening, and then uranium is eluted from the loaded resins. The stripped resins are recycled to recover additional uranium. However, ion-exchange resins with the necessary selectivity, durability, and capacity for copper RIP processes are not currently available.

Liquid ion exchange reagents have been developed for copper recovery processes (6-8). These reagents are widely used in copper solvent extraction processes, but clarified solutions are required. In processes where extraction characteristics of a liquid reagent are desired, but where processing conditions preclude its use, and when suitable ion-exchange resins are not available, extractants consisting of an inert solid impregnated with a liquid extraction reagent have been proposed to bridge this gap (9-11). Suggested suitable solids include elemental sulfur, organic polymers, clays, and activated carbons. In general, extraction characteristics of the liquid reagent are preserved but extraction kinetics are slowed and full loading of the liquid extractant is not achieved.

The Bureau of Mines prepared an extractant consisting of activated carbon impregnated with LIX-64N,[4] a copper selective liquid ion exchange reagent. Procedures were then devised for using this material for the recovery of copper from leach pulps prepared by the leaching of low-grade tailings. This reagent showed good selectivity for copper, the reagent loss was low, and the extractant was easily formulated from readily available materials. The solvent-impregnated carbon was then used in a cyclic RIP leaching process to recover copper from mill tailings. The dissolved copper in the leach pulp loaded on the carbon, the loaded carbon was recovered by screening, and the copper was then stripped from the carbon with spent electrolyte. Electrowinning produced high-purity cathodic copper. The stripped carbon was recycled to adsorb additional copper.

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

[4]Reference to specific products does not imply endorsement by the Bureau of Mines.

EXTRACTANT DEVELOPMENT

Preliminary laboratory tests showed that several available liquid ion-exchange reagents could be adsorbed on activated carbon. The tests also demonstrated that copper could be extracted from solutions using the solvent-impregnated carbons, and each of the adsorbed reagents retained its individual extraction and stripping characteristics. As in conventional solvent extraction, a hydrogen-ion cycle was utilized. Tests were made to determine the most suitable combination of carbon and reagent.

CARBON SELECTION

Copper extraction and stripping tests to select the most suitable carbon were conducted using LIX-64N as the adsorbed extractant. The liquid form of this extractant has been successfully used in several commercial solvent extraction operations, and therefore was chosen for carbon selection tests (6-7). The reagent can be adsorbed on carbon by simply mixing carbon and reagent for 5 min. Each of the carbon samples was impregnated to yield a product containing 26 pct LIX 64N (36 g reagent to 100 g carbon). The copper loading was determined by agitating each material with a pH2 copper sulfate solution containing 0.5 g/L Cu for 120 min. One hundred-ninety four grams of impregnated carbon was used per liter of aqueous solution. Copper stripping was accomplished by mixing the loaded carbon in an agitated vessel with 500 mL of solution containing 150 g/L H_2SO_4; the agitation time was 60 min. Results are presented in table 1.[5] The results showed that the best copper extraction was achieved with Darco minus 12- plus 20-mesh activated lignite carbon.

REAGENT SELECTION

After the selection of Darco minus 12-plus 20-mesh lignite carbon, tests were conducted to determine the most satisfactory liquid ion-exchange reagent. These results are presented in table 2. In each test, 194 g of Darco carbon containing 26 pct of the desired reagent was agitated in 1 L of a pH2 sulfate solution containing 0.5 g/L Cu and 0.5 g/L Fe. Stripping conditions were identical to those employed in the carbon selection tests. LIX-64N displayed the best combination of extraction and stripping characteristics with 78 pct extraction and 76 pct of the extracted copper stripped. LIX-64N also exhibited the best selectivity for copper over iron, which was desirable to minimize iron transfer

[5]The carbons listed in table 1 only represent those tested in our investigation; other brands could have been included. The carbons selected were readily available, off-the-shelf products.

TABLE 1. - Copper extraction and stripping characteristics of activated carbons impregnated with LIX-64N

Type of carbon	Particle size, mesh[1]	Cu extraction after 120 min, pct	Cu stripped after 60 min, pct[2]
Darco lignite.....	-12, +20	78	76
Pittsburgh coconut.....	-6, +16	46	70
Westates coconut.....	-15, +28	40	72
Nuchor bituminous coal..	-12, +40	11	82
Pittsburgh bituminous coal.....	-8, +30	8	65
Union Carbide lignite...	-12, +28	56	74

[1]Tyler sieve series.
[2]Percent of extracted copper.

to the copper electrolyte. Darco minus 12- plus 20-mesh lignite carbon impregnated with LIX-64N was chosen as the most suitable material for further testing.

TABLE 2. - Copper extraction and stripping characteristics of Darco lignite carbon impregnated with various ion-exchange reagents

Reagent	Cu extracted after 120 min, pct	Cu stripped after 60 min, pct[1]	Cu:Fe ratio extracted
LIX-64N..	78	76	174
LIX-34...	29	92	129
LIX-71...	43	71	142
Kelex 100	83	50	12
Kelex 125	78	42	8
Shell 529	66	84	61

[1]Percent of extracted copper.

After selection of Darco carbon and LIX-64N, several tests were conducted to increase the copper loading capacity of the impregnated carbon. The best results were obtained by impregnating the carbon to give a product containing 55 pct LIX-64N (63 g LIX to 100 g carbon), heating it to 150° C to drive off the inert solvent contained in the LIX-64N reagent, and reloading the carbon with additional LIX-64N (57 g of LIX to 100 g carbon). The final product obtained with this procedure contained 47.6 pct organic extractant by weight, and its maximum loading was 9.3 g of Cu per kilogram of carbon at a pH of 2.0. Impregnated carbons used in the previous selection tests had a loading capacity of only 3.9 g of Cu per kilogram. Even with a reagent content of 47.6 pct, infrared spectrophotometry and radioanalytic techniques demonstrated that loss of organic to the aqueous phase was very small; the aqueous phase contained less than 2 ppm of LIX-64N.

PRELIMINARY TESTS WITH CHINO TAILINGS

The tailings studied in the investigation were obtained from Kennecott Copper Co.'s Chino Mines operation in New Mexico. These minus 100-mesh tailings are typical of millions of tons of tailings scattered throughout the Western United States. They contained 0.24 pct total Cu, and 0.20 pct acid-soluble Cu. Tests were conducted to determine the feasibility of leaching the tailings in a pulp containing the impregnated carbon. The addition of H_2SO_4 during leaching was not necessary because of the weathered nature of the tailings and because LIX-64N exchanges about 1.5 lb of acid for each pound of copper extracted from solution. The best results were obtained with a tailings-to-carbon ratio of 1:0.382 and leaching for 120 min. The pulp density was 58 pct solids (tailings plus carbon). With these conditions, essentially all of the acid-soluble copper or 83 pct of the total copper was leached. Ninety-seven percent of the leached copper was extracted by the solvent-impregnated carbon, and the copper loading was 5.1 g/kg of carbon. The copper-loaded carbon was easily removed from the leached pulp by screening on a 28-mesh screen. Tests were then conducted to strip copper from the loaded carbon using spent electrowinning solution containing 150 g/L H_2SO_4 and 30 g/L Cu. The test results showed an increased stripping efficiency with increased time and temperature and decreased pulp density. An optimum stripping efficiency of 91 pct of the extracted copper was achieved by agitating the carbon for 1 h at 35° C and 33 pct solids.

Tests also were conducted to determine carbon and reagent losses through attrition. A 200-g sample of impregnated carbon was agitated in 1,200 mL of solution with 1,000 g of tailings. The power input was 1 hp per 1,000 gal of solution. After 48 h of agitation, the carbon loss was 0.054 lb/ton of tailings processed. The carbon was then agitated in an electrolyte solution for 48 h, and only 0.008 lb of carbon was lost per ton of tailings. The total loss was 0.064 lb/ton of tailings processed, or 0.016 lb/lb of copper. If the carbon loss was proportional to time, the loss for a 2 h leach followed by 1 h of stripping would be 0.0024 lb/ton of tailings.

CYCLIC TESTING

After completing the preliminary leaching and stripping tests, cyclic leaching, stripping, and electrowinning tests were conducted with the oxidizing tailings. Briefly, the process consisted of placing the solvent-impregnated carbon in a vessel containing tailings and water, and agitating the mixture with a marine propeller. As copper was leached from the tailings, it was extracted from solution into the carbon. The leached pulp and carbon were then separated by screening, the carbon was washed on the screen and dewatered by vacuum filtration, and the leached tails were discarded. The copper-loaded carbon was stripped with spent electrolyte, dewatered, and recycled to the leaching vessel. Meanwhile, the enriched electrolyte from stripping was advanced to an electrowinning cell where cathode copper was produced. Each unit operation was operated on a batch basis, and 44 processing cycles were completed.

LEACHING AND CARBON LOADING

The cyclic leaching, stripping, and electrowinning tests were conducted using 1,000 g of tailings per cycle. Impregnated Darco minus 12- plus 20-mesh carbon containing 47.7 pct adsorbed LIX-64N was employed at a carbon to tailings ratio of 0.382:1. The pulp density was 58 pct solids. A small amount of entrained electrolyte from the copper stripping section and the exchange acid associated with the adsorbed LIX-64N reported to the leaching vessel along with the stripped carbon. The pH near the beginning of the leach was 3.6; at the end of the 2-h leaching period, the pH was 2.1. The system was operated for 44 cycles, at which time steady-state conditions had been achieved. During this time, an average of 82 pct of the total copper or 98 pct of the acid-soluble copper was leached from the tailings. An average of 97 pct of the leached copper was extracted by the carbon, and the average loading was 6.6 g of copper per kilogram of carbon. The 97-pct extraction from the leach pulp is considerably higher than that obtained during the extractant development studies, which were made using clarified solutions. Observations suggest that the variation may be due to differences in wetting effects. When impregnated carbon was added to clarified solutions, some of the material was not wetted and tended to float; this restricted solid-solution contact. The carbon readily dispersed, however, when it was added to the leach pulps.

A flowsheet for the cyclic process along with relevant material balances are presented in figure 1. During each operational cycle, Chino tailings, recycle solutions, water, and the stripped carbon were charged to the leach-contact vessel and agitated for 120 min. The pulp was then screened on a 28-mesh screen; the recovered carbon was washed and then dewatered by vacuum filtration for 15 min to minimize dilution of the electrolyte

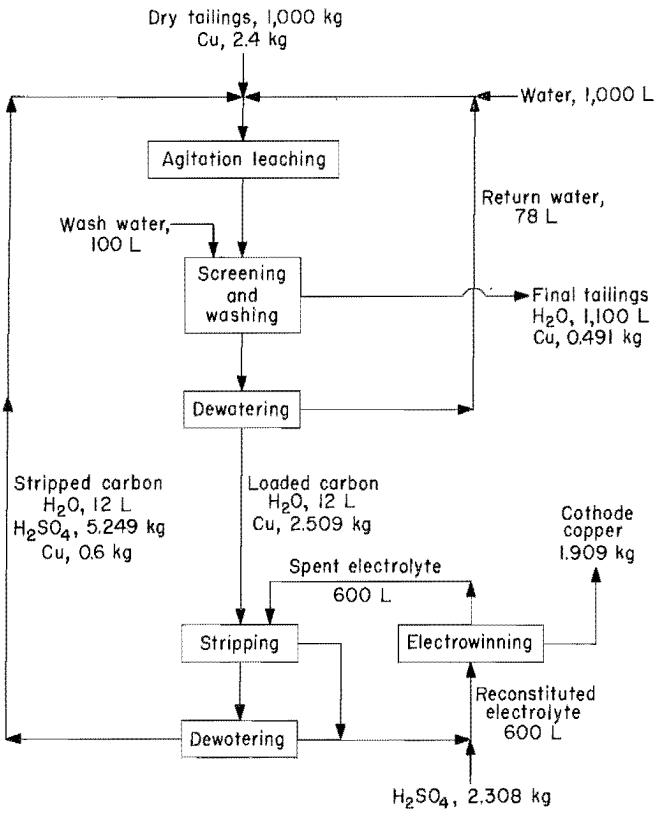

FIGURE 1. - Process flowsheet and material balances for recovering copper from mill tailings.

during the subsequent stripping operation. Before dewatering, the carbon contained only 0.236 g of moisture per kilogram; after dewatering, the advancing carbon contained only 0.031 g of moisture per kilogram of carbon.

CARBON STRIPPING AND ELECTROWINNING

Copper stripping was accomplished by mixing the copper-loaded carbon with 600 mL of spent electrowinning solution containing 150 g/L H_2SO_4 and 30 g/L Cu. Although 60 min of stripping was sufficient in preliminary tests, 90 min was used in the cyclic tests due to the increased copper loading, 5.1 versus 6.6 g/L of carbon. The stripping temperature was 35° C, and the average stripping efficiency was 92 pct of the extracted copper for the 44 cycles. The stripped carbon was dewatered for 12 min by filtration and returned to the leaching vessel. Each kilogram of recycled carbon contained 1.57 g of copper; approximately two-thirds of this copper content was due to entrained electrolyte, and the remainder was copper not removed during the stripping operation. The entrained electrolyte sufficed as an electrowinning bleed stream, thus the accumulation of iron and other impurities in the electrolyte was negligible.

The enriched electrolyte, which contained 33 g/L Cu and 146 g/L H_2SO_4, was advanced to an electrowinning cell containing five cathodes and six calcium-lead anodes. Copper foil 0.005 in thick was used for cathode starting sheets. The electrolyte was circulated through the cell at a rate of 0.05 gpm/ft^2 of cathode area, and the current density used was 12 A per square foot of cathode surface. When these conditions were used and the electrolyte was dosed with 60 ppm of cobalt, copper cathodes containing, in parts per million, 1.6 Pb, 3.6 Fe, 0.5 Sb, 1.5 Al, 1.9 Mn, and < 1 Mg were consistently produced.

SUMMARY AND CONCLUSIONS

Laboratory tests demonstrated that activated carbon impregnated with LIX-64N, a commercial solvent extraction reagent, is an effective copper extractant. Copper was recovered from low-grade oxidized mill tailings, and high-purity cathode copper was produced using an RIP-type process consisting of a simultaneous leaching-absorption step followed by stripping and electrowinning operations. During a 44-cycle test using Chino, NM, tailings, 98 pct of the acid soluble copper was leached from the tailings in a 2-h leach. The recycled impregnated carbon contained enough acid to leach the copper and provide a final pulp pH of 2.1. Ninety-seven percent of the leached copper was loaded into the carbon, giving an overall acid-soluble copper recovery of 95 pct. Ninety-two percent of the loaded copper was stripped from the carbon using spent electrowinning solution, while the remaining 8 pct was recycled back to the leaching section. No major processing difficulties were encountered; thus the process shows promise as a viable means of recovering copper from discarded tailings.

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